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certify that to the best of my knowledge and belief the  
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specification contained in the Priority Document No. Hei  
11-248349.

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(Translation)

[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] Polymer electrolyte fuel cell

[CLAIMS]

[Claim 1] A polymer-electrolyte fuel cell comprising at least a pair of gas diffusion electrodes sandwiching an ion conductive polymer-electrolyte layer therebetween and a pair of electroconductive gas channel plates sandwiching said gas diffusion electrodes therebetween, characterized in that said electroconductive gas channel plate comprises a metal having an electroconductive resin layer, in which electroconductive particles are dispersed, formed on at least part of a section of said metal in contact with said gas diffusion electrode.

[Claim 2] The polymer-electrolyte fuel cell in accordance with claim 1, characterized in that said electroconductive resin layer is provided with a basic organic substance.

[Claim 3] The polymer-electrolyte fuel cell in accordance with claim 1 or 2, characterized in that said electroconductive particles comprise a carbon powder having a specific surface area of not more than  $100 \text{ m}^2/\text{g}$  or a glassy carbon.

[Claim 4] The polymer-electrolyte fuel cell in accordance with claim 1, 2 or 3, comprising, between said base metal constituting said electroconductive gas channel plate

and said electroconductive resin layer, a layer comprising at least one metal or metal compound selected from Zn, Sn, Al, Cr compounds, Mo compounds and W compounds.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to polymer-electrolyte fuel cells useful as consumer co-generation systems and mobile power-generating appliances, particularly to a polymer-electrolyte fuel cell employing a polymer-electrolyte.

[0002]

[Prior Art]

Fuel cells simultaneously supply electricity and heat by electrochemically reacting a fuel such as hydrogen and an oxidant gas such as air at gas diffusion electrodes. Owing to the variety of electrolytes, there are several types of fuel cells. Polymer-electrolyte fuel cells employing polymers for electrolytes are constructed, for example, such that a polymer-electrolyte membrane having a  $-CF_2-$  skeleton and comprising sulfonic acids on the terminal ends of its side chains is adhered to electrode reaction layers mainly composed of a carbon powder carrying a platinum system metal catalyst and further, on the outer face thereof, a pair of electrode substrates having gas-permeable and electroconductive properties is arranged. In addition thereto, on the outer face thereof, electroconductive separator plates for

mechanically affixing an assembly of the electrode reaction layers and the electrolyte, and at the same time electrically interconnecting in series neighboring assemblies, are arranged. The separator plate has gas channels for supplying a reaction gas to the electrode and for conveying a surplus gas and water produced by the reaction of hydrogen and oxygen. Seals such as gaskets or sealants are arranged encompassing the gas channels and the electrodes, and they prevent direct intermixing and outward leakage of the reaction gases.

[0003]

To improve output voltage when it is employed as power-generating devices, generally, a plurality of individual single cells, composed of a polymer-electrolyte layer, gas diffusion electrode layers and separator plates having gas channels, are laminated. Each gas channel supplies a fuel gas such as hydrogen and air through a manifold from the exterior. Electric current generated at the electrode reaction layers is collected at the electrode substrates and taken out to the exterior through the separator plates. Separator plates are often formed from a carbon material having electroconductivity, gas-tightness and anticorrosive properties. Meanwhile, separators utilizing a metal material such as stainless steel have been examined from the viewpoints of ease of thinning the separator in addition to a molding property and a low cost.

[0004]

[Problem That the Invention Is to Solve]

Metal separators require strong corrosion resistance against long-term exposure to high-humidity gases, and besides suppressing contact resistance with the electrode also becomes important in order to improve the electric cells' power-generating efficiency. For instance, a metal separator employing stainless steel retains corrosion resistance by a passive state film, mainly composed of chromium oxide, formed on the surface thereof. Nevertheless, when a relatively thick passive state film is stably formed, high cell performance cannot be procured because the passive state film acts as an electrical resistor to increase the contact resistance. Conversely, under the condition that the passive state film is unstable, cell performance is reduced because corrosion current is increased and the electrode/electrolyte undergoes damage due to the metal ions leached.

[0005]

Likewise, a method of coating the metal surface by means of chemical-plating or vapor-depositing with an anticorrosive metal such as gold has also been investigated; however, lowering costs is difficult. Furthermore, forming a surface film by applying carbon paste, which is prepared with cellulose, polyvinyl chloride or epoxy resin as binder also has problems with the durability.

[0006]

Accordingly, there has been proposed a method of ensuring high corrosion resistance and contact

electroconductivity at a relatively low cost by securing electroconductive paths by penetrating the film for retaining corrosion resistance on the surface of the metal separator by changing a surface configuration of the contact portion or dispersing electroconductive powders of high hardness on the contact portion; however, performance degradation due to the metal ions leached during long operation is inevitable.

[0007]

[Means for Solving the Problem]

In order to solve above problems, a polymer-electrolyte fuel cell in accordance with the present invention comprises at least a pair of gas diffusion electrodes sandwiching an ion conductive polymer-electrolyte layer therebetween and a pair of electroconductive gas channel plates sandwiching the gas diffusion electrodes therebetween, characterized in that the electroconductive gas channel plate comprises a metal having an electroconductive resin layer, in which electroconductive particles are dispersed, formed on at least part of a section of the metal in contact with the gas diffusion electrode.

[0008]

Here, it is effective that a basic organic substance is disposed in the electroconductive layer having water repellency.

[0009]

Further, it is desirable that the electroconductive



particles comprise a carbon powder having a specific surface area of not more than  $100 \text{ m}^2/\text{g}$  or a glassy carbon.

[0010]

Furthermore, it is effective that there is disposed, between the base metal constituting the electroconductive gas channel plate and the electroconductive resin layer, a layer comprising at least one metal or metal compound selected from Zn, Sn, Al, Cr compounds, Mo compounds and W compounds.

[0011]

[Mode for Embodying the Invention]

In the polymer-electrolyte fuel cell, a gas to be supplied needs to be humidified in order to maintain the conductivity of the electrolyte membrane. In addition, water is produced at the cathode by galvanic reaction. Accordingly, water vapor is thought to condense, while the cell is in operation, in the area where the metal separators and the gas diffusion electrodes are electrically in contact. Carbon dioxide gas and various ionic impurities dissolve in the condensed water vapor to increase ion conductivity. As a result, corrosion of the metal separator develops. In the present invention, an electroconductive resin layer, which is made from a resin having water repellent or basic properties with electroconductive particles such as carbon powder dispersed therein, is provided on the surface of the metal separator.

[0012]

When the water repellent resin is employed, the condensed water having ion conductivity does not easily reach the metal surface due to water repellency of the resin layer; therefore, the corrosion, which is occurred by the condensed water reaching the metal separator through pin holes in the resin layer, is suppressed. Meanwhile, a corrosion resistance of corrosion resistant alloys such as stainless steel is maintained by a passive state oxide film formed on the surface. The stability of the passive state film varies according to the ambient pH, that is, the corrosion current increases in acidic atmospheres and the amount of ions leached will be large. Metal ions produced by such corrosion enter the electrolyte membrane in place of hydrogen ions, deteriorating the hydrogen-ion conductivity of the electrolyte membrane. Likewise, they are thought to lower the water content of the electrolyte membrane, and to impair the catalytic activity of platinum catalyst.

[0013]

As a result, cell performance is impaired during long operation. Consequently, if the basic resin is arranged on the surface of the metal separator, leaching of metal ions will be suppressed over the long term during operation of the cell because the pH on the surface of the metal separator is increased to allow the passive state film to be stabilized. Simultaneously arranging a metal, such as Zn, Sn or Al, whose ionization tendency is greater than the base metal, on the

surface of the base metal enables suppression of leaching of the base metal. Likewise, forming a film comprising an oxide or hydroxide of Cr, Mo or W also suppresses leaching of the base metal.

[0014]

On the other hand, in order to impart high electroconductivity, a sufficient quantity of the electroconductive powders must be mixed in the resin layer having electroconductive particles dispersed therein. Nevertheless, because metal ions created on the surface of the base metal leach to the exterior of the metal separator through the interface between the resin and the electroconductive particles, the specific surface area of the electroconductive powder is desirably small. Further, when carbon powder is used as electroconductive powder having high corrosion resistance, glassy carbon is superior to layered graphite (graphite). This is because metal ions are thought to disperse through the spacing of atomic layers in the layered graphite and leach to the exterior. In practice, it is preferable to balance electroconductivity and corrosion resistance (control of metallic ion elution) by mixing layered graphite having excellent electroconductivity and amorphous carbon such as glassy carbon.

[0015]

[Working Examples]

The present invention is thought to be inherently

effective on power-generating devices wherein electricity is taken out through electric contact between metal members to the exterior; however, examples utilizing a fuel cell, particularly a solid polymer fuel cell in which current density of contact surface is large and power-generating efficiency is largely affected by Joule loss, are concretely described.

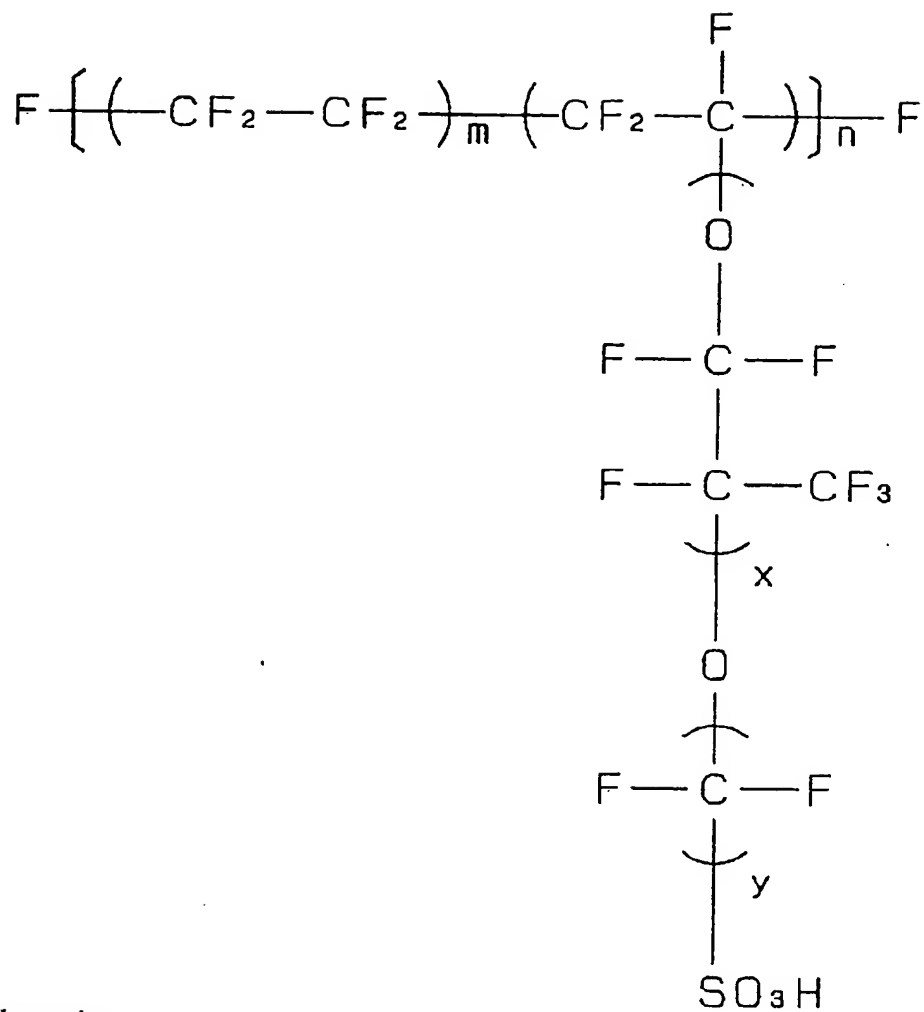
[0016]

(Example 1)

25 wt% platinum particles having a mean particle diameter of 30 Å were made carried on an acetylene black based carbon powder to give a catalyst for the reaction electrodes. A dispersion having been prepared by dispersing a perfluorocarbon sulfonic acid powder indicated by chem. formula (1) in ethanol was mixed with a solution having been prepared by dispersing the catalyst powders in isopropanol to yield a paste.

[0017]

[formula 1]



wherein:

m=5 to 13.5

n≠1000

x=1

y=2

[0018]

Next, on one surface of a carbon paper 300 μm in thickness, which would become the gas-diffusion electrodes,

was applied a carbon powder layer having been repellency-treated with an aqueous dispersion of polytetrafluoroethylene (PTFE), and it was dried; thereafter, the aforementioned catalyst paste was applied thereon to form an electrode reaction layer. A polymer-electrolyte membrane was sandwiched in a pair of the gas-diffusion electrodes, putting the electrode reaction layers inwards, and hot-pressed 30 sec. at 110 °C, to produce an electrolyte electrode assembly (MEA). In addition to carbon papers, carbon clothes obtained by weaving carbon fibers and a carbon felt obtained by molding a mixture of carbon fibers and a carbon powder to which an organic binder is added may also be employed as materials having flexibility for the gas diffusion layer.

[0019]

Separator plates were produced using stainless steel (SUS 316). Gas channel grooves for supplying a hydrogen gas which would serve as an active material and air and for expelling generated water vapor or drained gas were provided on the surface, of the separator, in contact with the gas diffusion electrode. A silicone rubber gasket, which would function as a gas sealant, was arranged on the periphery of the MEA, and the MEA was interposed in a pair of separator plates; thereby a unit cell was constructed. The electricity generated at the electricity generating part consisting of the electrolyte layer and the electrodes may be taken out from the metal separator plates to the exterior by way of the contact

surfaces of the gas-diffusion electrodes and the metal separators. In practice, a plurality of cells of this sort and cooling cells for flowing a cooling medium such as cooling water are laminated through separators to give a laminated cell to be used, but the present examples describe usefulness of the metal separator for the fuel cell of the present invention, exhibiting examples of a unit cell.

[0020]

In the resin layer to be arranged on the surface of the metal separator, fluoroelastomer was employed as resin binder. Fluoroelastomer and methylethyl ketone were added to flake graphite, and kneaded in a planetary ball mill to obtain an electroconductive paste. The electroconductive paste was applied on the stainless plate which would act as the separator plate, and dried. Likewise, an electroconductive paste obtained by adding an aqueous dispersion of a copolymer of fluoroethylene and fluoropropylene to flake graphite and kneading the same while partially vaporizing the water was formed into a thick film on the stainless plate.

[0021]

A cross sectional view of the surface portion of the stainless separator of the present invention is illustrated in Fig. 1. In Fig. 1, on the surface of a stainless substrate 1 (SUS 316) is formed a water repellent resin layer 2. In order to ensure electroconductivity of the resin layer, flake graphite is dispersed therein as electroconductive particles 3.

The electroconductive particles 3 are laid out such that they contact with each other or are adjacent enough to have electroconductivity. Carbon fibers 5 constituting a gas diffusion electrode 4 contact the electroconductive particles 3 at a current-carrying surface 6 of the metal separator. Even when a pinhole 7 is present in the water repellent resin layer 5, condensed water 8 rarely contacts the stainless substrate due to water repellency of the water repellent resin layer 5.

[0022]

For comparison purposes, acrylic resin and polyvinyl chloride were used as a resin binder, a solvent and flake graphite were added thereto to give an electroconductive paste, and a surface layer was made on the separator plate using it.

[0023]

In order to ascertain the water repellency of the electroconductive resin layer formed on the stainless plate, water contact angle was measured; consequently, the copolymer of fluoroethylene (TFE) and fluoropropylene (HFP) had the largest contact angle and the contact angles turned out to be smaller in the order of: fluoroelastomer > polyvinyl chloride > acrylic resin. Polymer electrolyte fuel cells were assembled using these four metal separators made of stainless steel and cell testing was performed. The electrode surface area was 25 cm<sup>2</sup> (5-cm square), 0.3 mg/cm<sup>2</sup> Pt was respectively applied on the air electrode side and the hydrogen electrode side as the



electrode catalyst, and "Nafion 112" was utilized as the electrolyte membrane.

[0024]

Fig. 2 indicates the changes of cell performance when durability testing was conducted at a current density of  $0.5 \text{ A/cm}^2$ . While performance deteriorated in a short time interval following the start of operation with the cells in which the acrylic resin and polyvinyl chloride were utilized as binder for the resin layer, no significant performance degradation was recognized even after 100 hours with the cells in which the fluoroelastomer and fluoropolymer were utilized though its initial performance was slightly low. Particularly, the performance degradation was small even after 200 hours with the cells employing the copolymer of fluoroethylene and fluoropropylene. Accordingly, it is determined that the larger the contact angle of the electroconductive resin layer formed on the current-carrying surface of the metal separator is, the higher the durability becomes; and that fluorine based resins have remarkable effect.

[0025]

(Example 2)

An example employing a basic resin, as a means of suppressing corrosion of the metal separator as well as leaching of the metal ions and degradation of the cell performance, is explained. An electroconductive paste was prepared using flake graphite as electroconductive particles,

a poly(amide-imide) resin as a resin binder and Cellosolve acetate as a solvent. An electroconductive resin layer was formed on the surface of the stainless separator by using the paste. The electroconductive resin layer was made to be approximately 50  $\mu\text{m}$  in thickness.

[0026]

As a result of the same cell durability testing at a current density of 0.5 A/cm<sup>2</sup> as in Example 1, it is proved that the durability, though an initial voltage turned out to be somewhat lower, improved greatly, compared to the cells indicated in Fig. 2 in which the acrylic resin and polyvinyl chloride were utilized as the binder for the resin layer. The reason that the initial voltage turned out to be lower is thought to be because electroconductivity thereof is lower than that of the resin layer in which the acrylic resin and polyvinyl chloride are utilized; however, it can be improved by optimizing the type, the quantity, and the forming method of electroconductive particles.

[0027]

It is thought that if the polymer material constituting the resin has an amide structure therein, the oxide film on the adjoining metal surface is stabilized by the effect of an electron pair of the nitrogen atom and thereby to improve the corrosion resistance. The resins for improving corrosion resistance by contacting the metal surface preferably have a structure which provides basic property such

as an amino group. It is also effective to employ particles composed of metal, metal oxides, metal nitrides, metal carbides or the like that are to a certain extent anti-corrosive such as titanium fine powder, ruthenium oxide, titanium nitride or titanium carbide, though both examples 1 and 2 used flake graphite as electroconductive particles.

[0028]

(Example 3)

The cell in which a copolymer of fluoroethylene and fluoropropylene was utilized in Example 2 was operated more than 500 hours; consequently, the output voltage dropped 10% or more compared to the start. Next, the electroconductive particle formed by comminuting, instead of flake graphite, glassy carbon into approximately 20  $\mu\text{m}$  mean particle diameter was used. Likewise, metal separators, in which acetylene blacks having different specific surface areas were employed, were utilized as constituent member to manufacture cells.

[0029]

As a result of the same cell testing as in Example 1, it is determined that the voltage deterioration of the cell employing glassy carbon is suppressed to less than 3% even after 500 hours of operation. However, since electroconductivity is lower than flake graphite, output voltage itself is not so high. The cell testing utilizing acetylene black has also revealed that durability is improved when specific surface area is not more than 100  $\text{m}^2/\text{g}$ .

Durability is deteriorated, on the contrary, when specific surface area is too large.

[0030]

It is thought that durability will be ensured while maintaining electroconductivity by employing mixtures of various carbon powders besides the aforementioned constitution.

[0031]

These examples utilized SUS 316 as the metal for the separator. In order to minimize the cell performance degradation due to the contact resistance increase resulting from the passive state film on the separator, it is preferable to previously remove the oxide film on the metal separator before the electroconductive resin layer is formed. Even when a metal other than stainless steel, such as carbon steel, is used, improvement effect on durability is presumably high. Metal materials, which are easy to be processed but flawed regarding corrosion resistance, such as aluminum are also applicable.

[0032]

(Example 4)

For the purpose of further improvement in durability, various metal layers which improve durability were formed on the surface of the metal substrates constituting separators. First, Zn, Sn, or Al was applied on the surface of carbon steel at a thickness of several  $\mu\text{m}$  and then an electroconductive resin layer using a copolymer of

fluoroethylene and fluoropropylene or an electroconductive resin layer using a basic resin was formed. Likewise, chromium oxide, molybdenum oxide or tungsten oxide was applied on the carbon steel by a sputtering method and then an electroconductive resin layer was formed thereon. As electroconductive particles to be dispersed in these electroconductive resin layers, glassy carbon which had been comminuted into approximately 20  $\mu\text{m}$  mean particle diameter was used. Cells were manufactured by employing metal separators having been experienced these surface treatments, and the same durability testing as in Example 1 was performed.

[0033]

As a result, for whichever cell, the output drop following 500 hours of operation was suppressed to the 2% range. However, the initial property itself was slightly low regarding the cell utilizing the metal separator with a layer comprising Al or other oxides formed thereon. This is thought to originate in degradation of electroconductivity due to addition of an oxide layer. Durability can be improved while maintaining the initial property to a certain extent by improving the thickness and the shape of the metal layer or the oxide layer which is formed in order to improve durability.

[0034]

In order to verify usefulness of the structure shown in the present example, experiments were further performed using resin binders having low water repellency and low basic

property such as polyvinyl chloride. As a result, it is revealed that the durability improves by forming a metal layer or an oxide layer between the metal substrate and the electroconductive resin layer, which constitute the separator, even when the water repellency and basic property of the electroconductive resin layer are low.

[0035]

The relations between particle diameter of the electroconductive particle dispersed in the electroconductive resin layer which was used from Example 1 through 4 and improvement in cell durability was investigated using glassy carbon particles. Powders having mean diameters of 5, 10, 25 and 50  $\mu\text{m}$  were obtained by pulverizing glassy carbon in a ball mill, they were dispersed in the electroconductive resin layer, a cell was constituted, and durability testing was conducted. As a result, it is determined that the smaller the particle diameter of glassy carbon is and the greater the content in the resin layer is, the higher the initial performance of the cell becomes; and that the larger the particle diameter is and the less the content is, the higher the durability thereof becomes.

[0036]

#### [Effects of the Invention]

The present invention enables long-term control of increase in contact resistance and output deterioration due to corrosion in a fuel cell.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG.1] A schematic sectional view of a separator surface in Example 1 of the present invention.

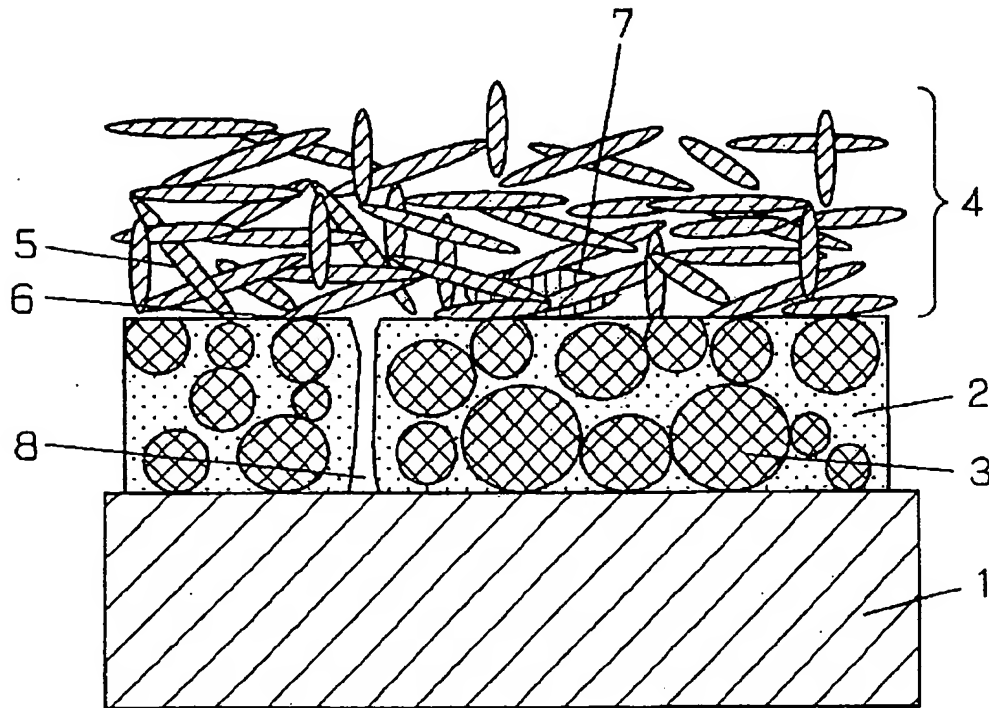
[Fig.2] A plot indicating results of a durability test on a cell manufactured in other examples of the present invention.

[Explanation of Reference Numerals]

- 1 Stainless substrate
- 2 Water repellent resin layer
- 3 Electroconductive particle
- 4 Gas diffusion electrode
- 5 Carbon fiber
- 6 Current-carrying surface of metal separator
- 7 Pinhole
- 8 Condensed water

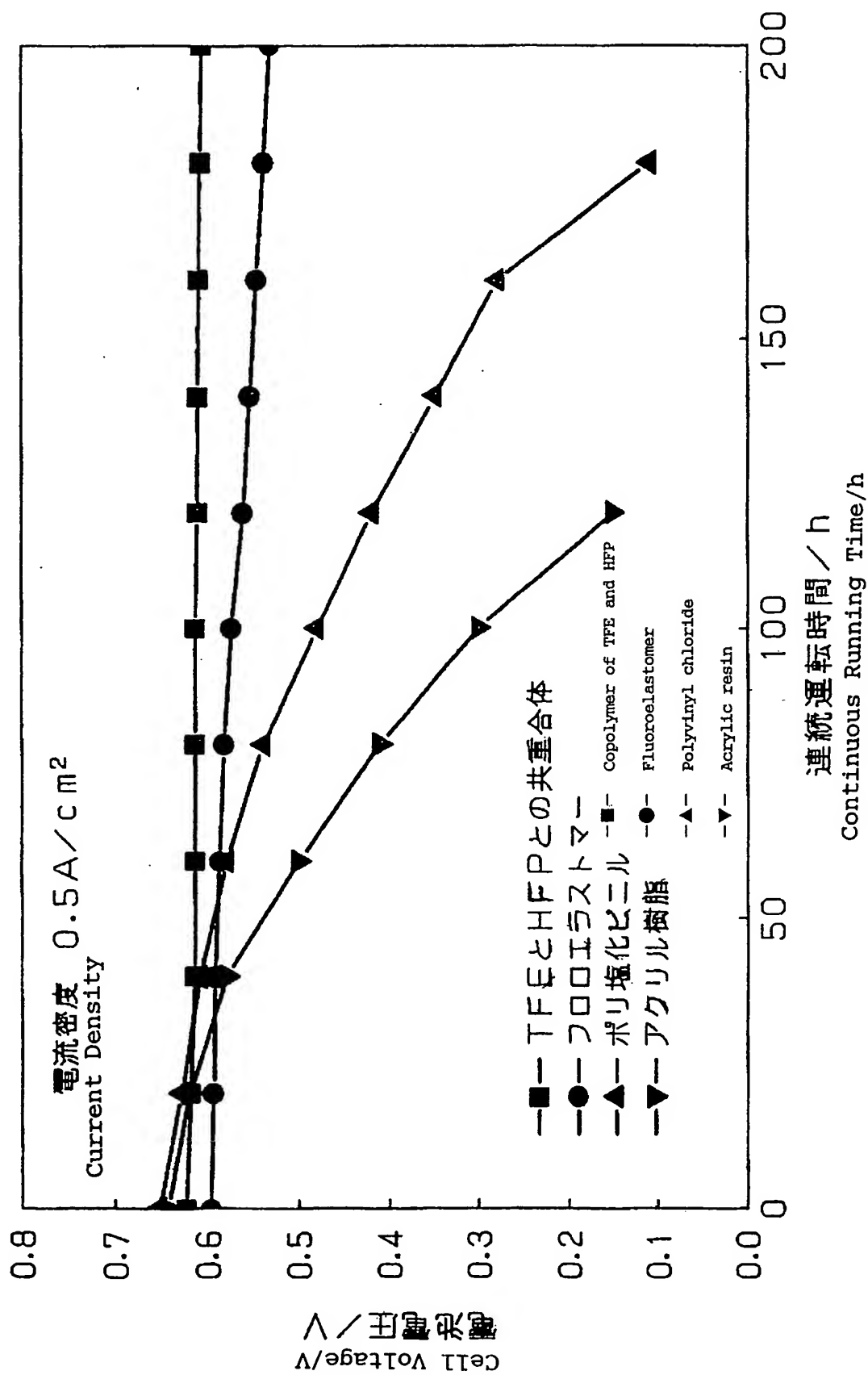
【書類名】 図面 [DOCUMENT NAME] Drawings

【図1】 [FIG. 1]





【図2】 [FIG. 2]



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(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECTIVE] In fuel cells employing metal separators, performance deteriorated due to contact resistance between the separator plate and the electrode, and to metal ions leached from the metal separator. The deterioration of the performance was controlled by a gold plate or the like, but the cost was large.

[SOLVING MEANS] Electroconductive particles such as carbon are dispersed on the surface of the metal substrate which constitutes the separator plate using a binder having high water repellency or basic property. Thereby, leaching of metal ions due to metal corrosion is reduced while increase in contact resistance between the gas diffusion electrode and the separator plate are controlled to ensure durability. Since the resin having high water repellency cannot have meniscus of condensed water and the basic resin makes the oxide film on the adjoining metal stable, metal corrosion can be suppressed.

[SELECTED DRAWING] FIG. 1